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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY
CHEMICALLY INITIATED ELECTRON-EXCHANGE LUMINESCENCE.(U)
NOV 80 G B SCHUSTER, K A HORN

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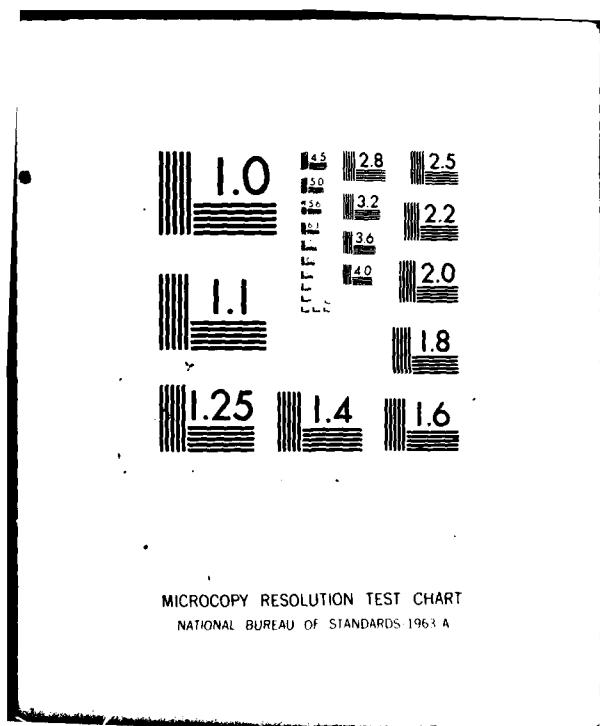
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Chemically Initiated Electron-Exchange Luminescence.

by

10) Gary B. Schuster ~~and~~ Keith A. Horn

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School of Chemical Sciences

University of Illinois

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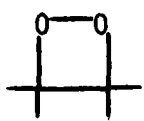

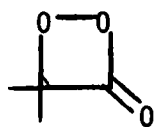

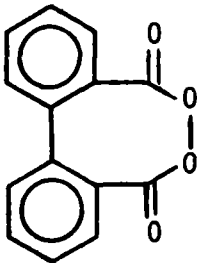
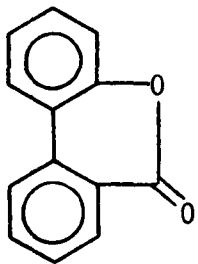
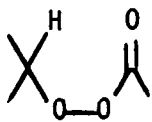

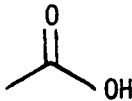
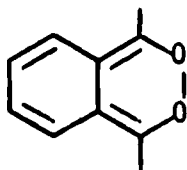
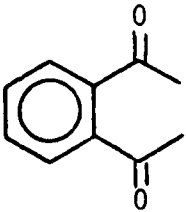
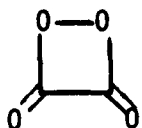
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Chemiluminescence from organic molecules is an end result of a series of complex chemical and physical transformations. These transformations convert the potential energy contained in the chemical bonds of the reactants to radiant energy in the visible region of the electromagnetic spectrum. Since the discovery of the first efficient chemiluminescent reactions there has been considerable effort to unravel the details of the mechanism for this energy conversion. In broadest terms, what has evolved is a tripartite division of interrelated processes. The first of these three processes is the preparation of a reagent, or an intermediate, whose further reaction is sufficiently energetic to generate a photon of visible light. This is not a trivial problem. The visible spectrum extends from ca. 400-700 nm. Thus the total energy released by the chemical process must be greater than 40 kcal/mole. It is therefore not surprising to find that most known chemiluminescent systems involve, as this key reagent or intermediate, an organic peroxide. There are few other simple functional groups known that present as favorable an energy balance as the conversion of a peroxide to two carbonyl group containing products. Thus, by and large, the objective of the synthetic portion of the investigation of chemiluminescence has been to prepare a peroxide which has a reaction path for formation of carbonyl groups available. Some of the successful applications of this synthetic strategy are presented in general form in Table 1.

The second process in the prototypical chemiluminescence sequence is the conversion of the appropriate reagent or intermediate formed in the synthetic step to an electronically excited state. This is the process whereby

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Table 1

Peroxide	Products	ΔH_r^a (kcal/mole)
	2 	-67.5
	 + CO ₂	-91.3
	 + CO ₂	-71.1
	 + 	-58
		-87
	2CO ₂	-120

^aAll values are estimates based upon Group Equivalent calculations. Thus the relative magnitudes of the set may be more meaningful than the actual value.

the actual conversion of chemical potential energy to the energy of electronic excitation takes place. This process is the heart of all chemiluminescent reactions. The details of structure and reactivity that determine the mechanism and efficiency of this the chemiexcitation step are at the center of our studies, and they are the major topic of this chapter. Below, we will briefly introduce some of the mechanisms that have been observed to facilitate the conversion of organic peroxides to electronically excited state products with special emphasis on the chemically initiated electron-exchange luminescence (CIEEL) mechanism (Schuster 1979)

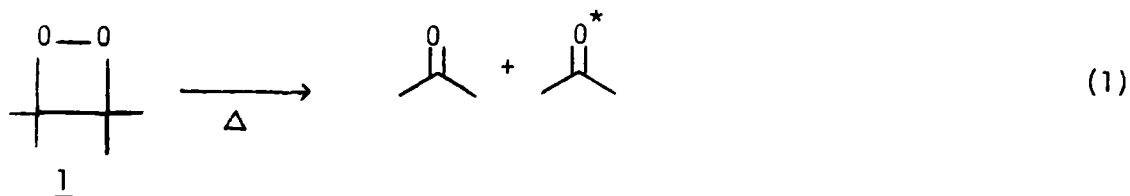
The final process in our triumvirate is the emission of light from the excited state formed in the chemiexcitation step. Since very few organic molecules phosphoresce with more than miniscule efficiency in fluid solution, it is a critical necessity for efficient chemiluminescence to form either initially or eventually a high yield of the electronically excited singlet state. This objective has so far proved to be difficult to achieve, and it is an area of current research. In most instances, once the excited state is formed it behaves just as the state that results on photoexcitation does under the same conditions. Thus information gained from investigation of the photochemistry and photophysics of these systems is usually directly applicable to the chemiluminescence. Indeed, photophysical energy transfer from the first formed excited state to an added acceptor molecule distinguishes direct chemiluminescence, where the former is the emitting species, from indirect chemiluminescence, where an excited energy acceptor is responsible for light emission.

The three processes of organic chemiluminescence, synthesis, excitation, and emission each present many intriguing areas for study. Our emphasis has been on the excitation step and the results of that investigation are described below.

Mechanism of the Excitation Step

The chemiexcitation process is the one single feature that distinguishes reactions that generate visible light from all other chemical transformations. For chemiluminescent organic peroxides two distinct excitation mechanisms have been found to operate. The first is a unimolecular thermally activated homolytic cleavage process typified by simple alkyl substituted 1,2-dioxetanes. The second is centered around the eventual annihilation of oppositely charged radical ions which are themselves formed in chemical reactions.

There have been numerous studies of dioxetane chemiluminescence. Among the important questions probed is the precise timing of the bond cleavage and the electron promotion for this case. This has been studied both experi-



mentally and computationally. Two limiting mechanisms have evolved. The first is a concerted cleavage of the O-O and C-C bonds to form directly the carbonyl containing compounds. The second is a stepwise dissociation of the dioxetane ring: first the O-O bond breaks resulting in a biradical, then the C-C bond cleaves to give the carbonyl group products. Although there is no direct evidence absolutely ruling out one or the other of these possibilities, the weight of the available experimental and theoretical results appears to bear heavily on the side of the step-wise process. These results were recently reviewed (Horn et. al., 1978) and will not be discussed further here. The unimolecular thermal cleavage route for chemiexcitation apparently occurs in systems other than 1,2-dioxetanes as well. For example, electronically excited substituted benzenes result from the thermolysis of substituted bicyclo[2.2.0]hexadienes (Dewar benzenes) (Lechtken et. al., 1973). Also many of the less well studied weaker

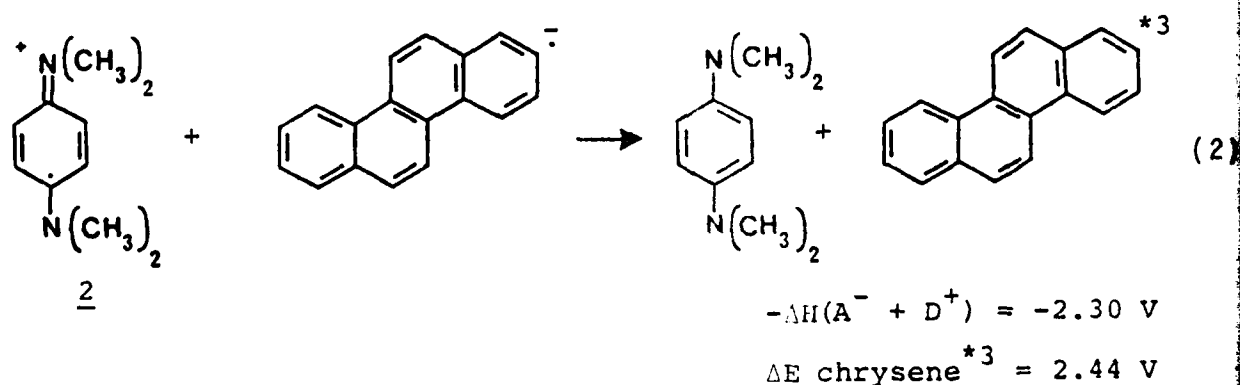
chemiluminescent reactions may proceed by this mechanism.

The second general mechanism for chemiexcitation of organic peroxides centers around exergonic one electronic transfer reactions. A considerable number of chemical oxidation-reduction reactions are known to occur via mechanisms in which one or more steps involve a one-electron transfer. A significant number of these electron-transfer processes result in chemiluminescence. The efficiencies of these chemiluminescent processes range from the order of 10^{-9} to those where the yield of excited states may approach 100%. The relative simplicity of the excitation step of the electron-transfer reaction has made it a prime candidate for study, both experimentally and theoretically. We present here a series of known chemiluminescent electron-transfer reactions which provide a basis for the recently proposed chemically initiated electron-exchange luminescence (CIEEL) mechanism.

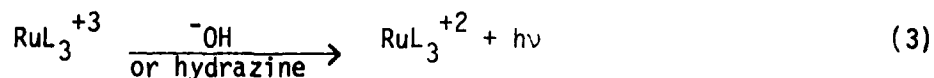
One of the simplest observed chemiluminescent electron-transfer reactions is the recombination of a solvated electron with the radical cation of naphthalene. It was found (Brocklehurst et. al., 1964) that when naphthalene is irradiated with γ -rays in a matrix at 77°K and then the matrix is softened by warming, emission occurs from both the lowest excited singlet and triplet states of naphthalene. The electron ejected by photoionization apparently remains trapped in the matrix until the temperature is raised. The "annihilation" of the radical cation and electron provides the energy necessary to produce the excited states which are detected by their characteristic emissions. The reaction of solvated electrons (produced by pulse radiolysis) with aromatic hydrocarbon radical cations has also been shown to be chemiluminescent (Itaya et. al., 1976).

The first example of a chemical counterpart to the photoionization luminescence was reported nearly simultaneously (Chandross et. al., 1964). The oxidation of sodium or potassium 9,10-diphenylanthracenide with bromine, chlorine, benzoyl peroxide,

oxalyl chloride or 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene results in emission from the first excited singlet state of 9,10-diphenylanthracene. Similarly, the oxidation of sodium naphthalenide by alkyl halides probably proceeds by an electron-transfer (Haas et. al., 1967). Since these initial studies numerous examples of radical anion oxidations have been observed to be chemiluminescent (Zweig, 1968). Particularly common are the oxidations of aromatic radical anions by Wursters Blue cation (2). One such example, the oxidation of chrysene radical anion, is shown in equation 2 (Weller et. al., 1967). Chemiluminescence can also be produced by the

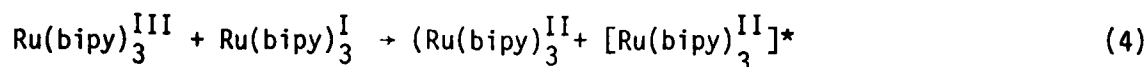


electron-transfer reactions of inorganic complexes with either charged or neutral reductants (Hercules, 1969). Thus, the one-electron reduction of ruthenium(III) chelates by either aqueous base or hydrazine results in light emission from the reduced complex. The overall reaction is shown in equation 3. The ligand (L) may be bipyridyl or a substituted phenanthroline. The mechanism



involves a complex series of reactions in which several high energy transient species are formed and are responsible for the chemiexcitation process.

A related, relatively more simple, chemiluminescent trisbipyridyl ruthenium(III) reaction is the one reported by Bard (Tokel-Takuoryan, et. al., 1973). This disproportionation reaction may have considerable implications for the mechanism postulated for the chemiluminescent reduction of trisbipyridylruthenium (III) by



hydrazine.

Much of our present understanding of the chemiluminescence that results from the annihilation of oppositely charged radical ions has come from electrogenerated chemiluminescence (ECL) experiments. One reason for this is that the generation of the highly reactive radical ion species can be easily and selectively carried out at electrodes. The first observation of chemiluminescence from the electrolysis of mixed solutions of aromatic hydrocarbons were reported independently (Rauhut et. al., 1964, Hercules, 1964, Santhanam et. al., 1965). Since then, a large number of ECL systems have been observed and studied. This subject is reviewed in Chapter of this volume. For the general annihilation reaction of radical anion (A^-) with radical cation (B^+) (equation 5), the free energy of the reaction can be calculated using the



electrochemical potentials for the individual couples. The free energy in

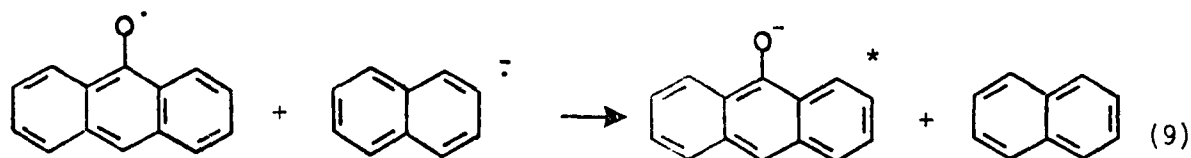


electron volts is thus described by

$$\Delta G^\circ = E^\circ(A/A^\cdot) - E^\circ(B^\cdot/B) \quad (8)$$

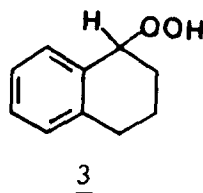
If the energy required to reach the emitting state of either A or B is less than $-\Delta G^\circ$ for the annihilation, then chemiluminescence is possible.

Several cases of suspected chemiluminescent electron-transfer reactions are less well defined than the ECL systems. Examples include the series of chemiluminescent autooxidation reactions of various 9-substituted acridines (under conditions of strong base and oxygen in dimethyl sulfoxide) and the chemiluminescent electron transfer from potassium naphthalenide to a proposed transient oxy radical of anthracene, equation 9 (Rapoport et. al., 1972).

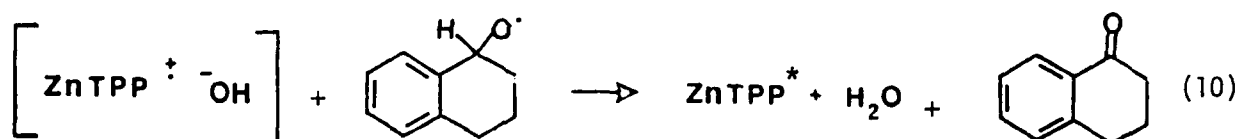


Chemically Initiated Electron Exchange Luminescence of Peroxides (CIEEL)

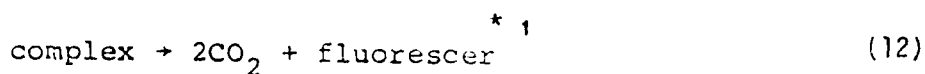
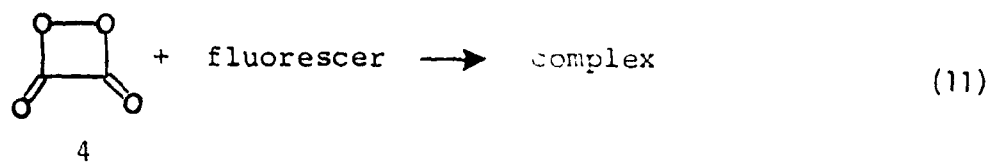
The extensive involvement of peroxides in chemiluminescent reactions and the ease of reduction of many organic peroxides would seem to make them prime candidates for use as electron-transfer chemiluminescent reagents. However, prior to 1977 only a very few chemiluminescent systems involving organic peroxides were even postulated to proceed by an electron-transfer mechanism. The first of these reactions to be reported is the reaction of tetralin peroxide (3) with zinc tetraphenylporphine (Linschitz, 1961). The last step in the rather involved light producing reaction pathway was postulated to be the reduction



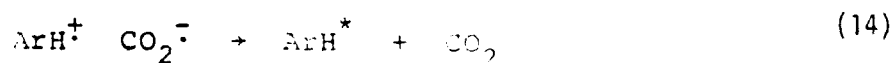
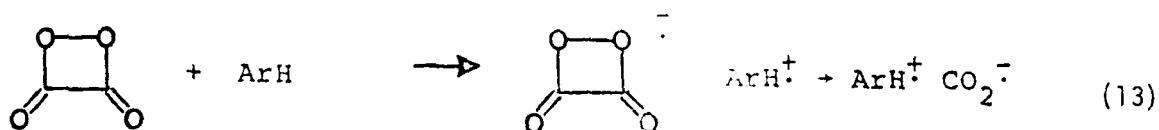
of the zinc tetraphenylporphine (ZnTPP) radical cation by an alkoxy radical, equation 10. A considerably more well defined case is found in the work



of Rahut on the chemiluminescent reaction of hydrogen peroxide with substituted aryl oxalates (Rahut et. al., 1967). These reactions have been postulated to generate 1,2-dioxetanedione (4) as the high-energy chemiluminescent intermediate. In the presence of added fluorescer molecules efficient chemiluminescence is observed. Moreover, the lifetime of the chemiluminescent intermediate is apparently shortened by the presence of some aromatic fluorescers (e.g., rubrene). More significantly, the chemiluminescence efficiency does not correlate with either the fluorescence efficiency or the singlet energy of the added fluorescer. Rahut explained these results by postulating the transient charge transfer complex between the 1,2-dioxetanedione and the added fluorescer (equations 11 and 12). Later McCapra (McCapra, 1973) suggested an interesting



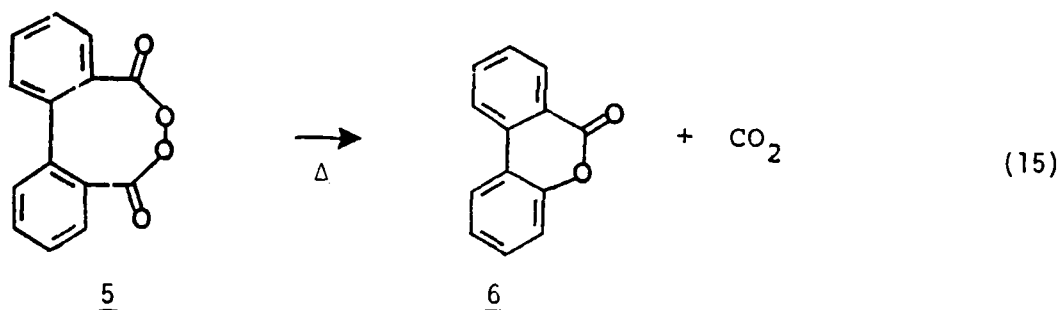
modification of this mechanism having certain processes in common with other examples of electron-transfer luminescence. The key feature of this proposal is a one-electron transfer from the aromatic hydrocarbon fluorescer to the 1,2-dioxetanedione intermediate, equation 13.



The actual excitation was then suggested to occur in the annihilation of the aromatic hydrocarbon radical cation ($\text{ArH}^{\cdot+}$) with the carbon dioxide radical anion generated by decarbonylation of the 1,2-dioxetanedione radical anion. Relatively little is known about the excitation mechanism in this system primarily because of the lack of evidence for and the instability of the presumed 1,2-dioxetanedione intermediate.

Chemiluminescence of Diphenoyl Peroxide

The first well-defined example of a specific chemiluminescent electron-exchange reaction between an organic peroxide and suitable electron donors was reported recently (Koo et. al., 1977). It was found that diphenoyl peroxide (5) reacts with certain aromatic hydrocarbons to form the excited singlet state of the hydrocarbon. The thermal reaction of diphenoyl peroxide to form benzocoumarin (6) and CO_2 is exothermic by ca. 70 kcal/mol. This reaction enthalpy combined with the activation energy of ca. 24 kcal/mol makes available approximately 94 kcal/mol for the formation of excited states. Since the singlet energy of benzocoumarin is ca. 88 kcal/mol, direct production of excited state benzocoumarin is permissible. However, no chemilumines-



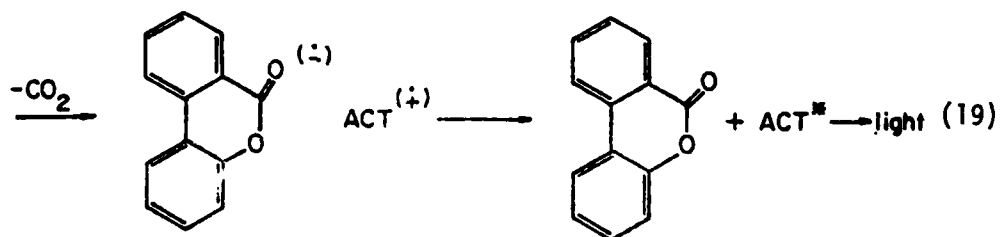
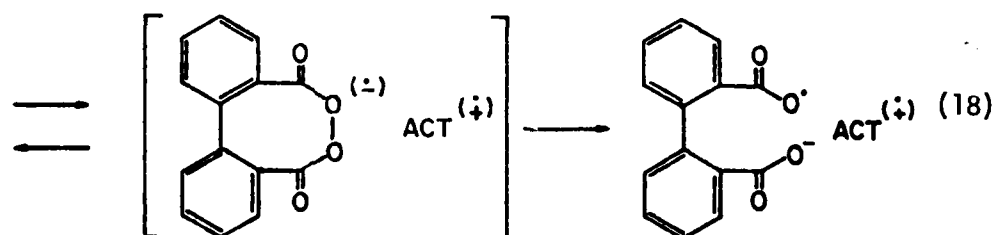
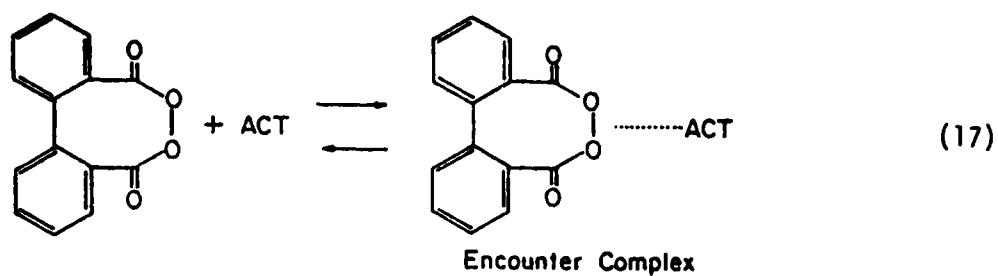
cence is detected from solutions of diphenoyl peroxide (and 9,10-dibromoanthracene (DBA) or biacetyl). In contrast to this striking lack of chemiluminescence by such a highly exothermic peroxide decomposition in the presence of DBA, solutions of 5 and more easily oxidized aromatic hydrocarbons such as rubrene were found to produce a bright, readily-seen chemiluminescence. Further, the added aromatic hydrocarbon catalyzes the decomposition of the diphenoyl peroxide though no ground state complex is detected. The dependence of the observed rate constant for the chemiluminescence decay on the added aromatic hydrocarbon (ArH) follows the simple kinetic expres-

sion in equation 16. Here k_1 represents the rate constant for the unimolecu-

$$k_{\text{obsd}} = k_1 + k_{\text{CAT}}[\text{ArH}] \quad (16)$$

lar decomposition of diphenoyl peroxide and k_{CAT} is the rate constant for the bimolecular reaction of diphenoyl peroxide with the added aromatic hydrocarbon. Importantly, the activation energy for the catalyzed decomposition is the same as the activation energy for the light-generating reaction. This implies that these two reactions have the same rate-determining step. Of prime significance is the observation that the only consistent correlation between the observed magnitude of the bimolecular rate constant (k_{CAT}) and various aromatic hydrocarbons is an inverse correlation of $\ln k_{\text{CAT}}$ with the one-electron oxidation potential of the added hydrocarbons. No other parameter (singlet energy, triplet energy, structure, etc.) provide any reasonable correlation. In Figure 1 is presented the mechanism postulated to explain the experimental observations for the chemiluminescent decomposition of diphenoyl peroxide. This mechanistic pathway is designated in general as chemically initiated electron exchange luminescence (CIEEL).

The first and rate-determining step of the CIEEL mechanism involves an activated electron transfer from the aromatic hydrocarbon ("chemiluminescent activator") to diphenoyl peroxide. The precise details of the electron-transfer process are, of course, unknown. However, a reasonable process, patterned after Marcus electron transfer theory, proceeds through an encounter complex between the activator and peroxide that is in equilibrium with reagents in bulk solution. In most cases the position of this equilibrium is apparently controlled by diffusion. However, with certain organometallic compounds (see below) the



26

Figure 1. The CIEEL mechanism for the thermal reaction of diphenoyl peroxide (2) with ground state aromatic hydrocarbons (activators).⁸⁵

complex is stabilized. Thermal activation of the encounter complex through collisions with solvent molecules forces the system along a reaction coordinate taken to be the O-O bond length. At a certain O-O bond distance, dependent upon the oxidation potential of the activator, there is an avoided crossing of the reactant potential energy surface with that of the electron transferred state. This crossing point represents the transition state for the reaction. A structure for this transition state is shown in the square brackets in equation 18. The reaction coordinate just described is shown schematically in Figure 2. These considerations lead to the conclusion that the experimentally determined k_{CAT} is made up of the equilibrium constant (K_{12}) for complex formation and the rate constant for electron transfer (k_{ACT}) if the electron transfer is irreversible. The electron-transfer

$$k_{CAT} = K_{12} k_{ACT} \quad (20)$$

induced decomposition readily explains the correlation of k_{CAT} with the one-electron oxidation potential of the various activators and suggests a mechanism for the induced decompositions of peroxides by nucleophiles and metal ions. The magnitude of k_{ACT} is simply described by the Polanyi type relationship between the free energy of the electron transfer and the activation energy of the reaction; of equation 21 where E_{ox} is the oxidation potential of the activator, E_{red} is the reduction potential of the peroxide

$$k_{ACT} = A \exp\left(-\alpha\left(E_{ox} - E_{red} - \frac{e^2}{\epsilon R_0}\right)/RT\right) \quad (21)$$

e is the electronic charge, ϵ is the dielectric constant of the solvent, R_0 is the distance between the ions at the transition state, and α is a constant, related to the transfer coefficient of electrode reactions, that

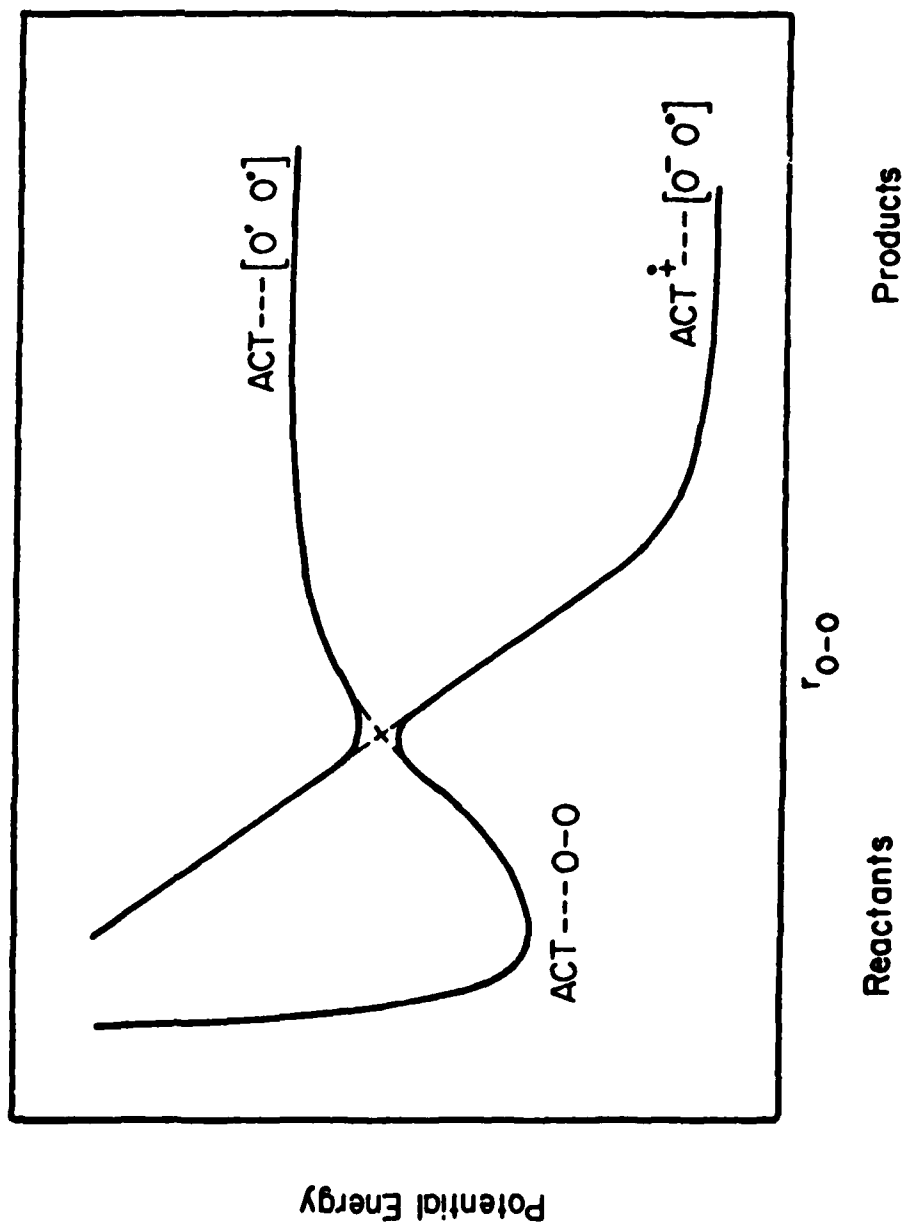


Fig. 2

can have a value between zero and one (Schuster, 1979). For diphenoyl peroxide, has a value of ca. 0.3. Thus, for any given solvent at constant temperature, the magnitude of the bimolecular rate constant for reaction of diphenoyl peroxide is predicted to depend only on the oxidation potential of the activator.

The initial electron transfer peroxide bond cleavage sequence leaves diphenate radical anion and activator radical cation. Loss of CO_2 and cyclization of the radical anion generates the powerful reducing agent, benzocoumarin radical anion. These cage radical ions are postulated to annihilate and generate the electronically excited singlet state of the aromatic hydrocarbon. In competition with the decarboxylation and subsequent charge annihilation is the separation of the radical ions by diffusion. Evidence that the light generating processes occur within the solvent cage is provided by the lack of a significant effect of oxygen on the chemiluminescent efficiency ($10 \pm 5\%$), and the increase of excited state yields in viscous solvents (dimethyl- and di-*n*-butyl phthalate). Further supportive evidence for this mechanism derives from the observation of thermally generated emissive exciplexes of benzocoumarin and triphenylamine or *N*-phenyl-carbazole from diphenoyl peroxide. Thus, the exciplex in these cases is the initially formed excited state species.

Confirmation that radical ion intermediates are involved in the chemiluminescence of diphenoyl peroxide comes from an analysis of some laser flash spectroscopic studies (Horn et. al., 1979). Pulse excitation of the electron donor enables identification of the intermediate reaction products by their characteristic absorption spectra. This technique also permits the direct measurement of the rate of the reaction.

Electronic excitation of, for example, an aromatic hydrocarbon produces an excited state which is both a better reducing and a better oxidizing agent

than the ground state. The redox potentials for electronically excited states, while not easily measured directly, can be accurately estimated from ground state redox data and the energy of the optical transition according to equation 22. For example, the oxidation potential of ground state pyrene is 1.33 V (vs. SCE) and the singlet energy is 3.34 eV. Thus the oxidation potential of excited singlet pyrene ($\text{Py}^{\star 1}$) is ca. -2.00 V (vs. SCE).

$$E_{\text{ox}}^{\star} = E_{\text{ox}} - E^{\star} \quad (22)$$

When $\text{Py}^{\star 1}$ is generated by pulse excitation with a nitrogen laser in the presence of diphenoyl peroxide in acetonitrile solution a rapid reaction takes place that results in the quenching of the $\text{Py}^{\star 1}$ fluorescence. An absorption spectrum of the reaction mixture recorded 200 ns after the excitation pulse reveals the presence of pyrene radical cation. Similarly, other excited electron donors react with diphenoyl peroxide to generate the corresponding radical cations.

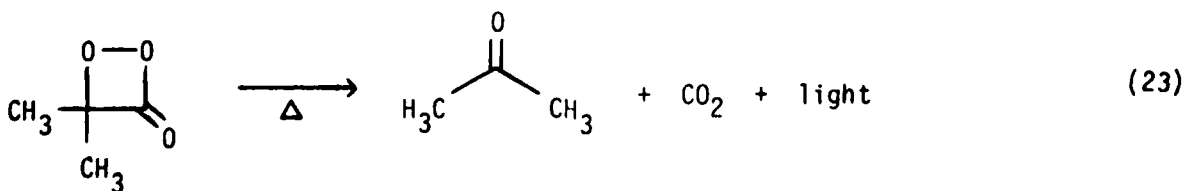
To relate the behavior of the ground state activators, used in the chemiluminescence experiments, to the excited state electron donors, employed in the pulsed-laser studies, it is necessary to compare the kinetics of the reaction in both cases. According to the CIEEL mechanism, the sole predictor of the rate constant for reaction between diphenoyl peroxide as an electron donor, in a given solvent, is the one electron oxidation potential of the activator. Thus, if electron transfer is the rate limiting step in the chemiluminescence of diphenoyl peroxide, then the rate constant for reaction of the electronically excited activators, where electron transfer has been demonstrated unambiguously by spectroscopic methods, should correlate with the rate constants observed for the ground-state activators. The rate con-

stants for singlet excited activators were determined by monitoring the fluorescence lifetime following pulse excitation; and for the triplet activators by following the triplet-triplet absorption spectrum. The correlation of the rate constants for ground and excited state activators with oxidation potential shown in Figure 3 is excellent. The single predictor, over a 10⁴ fold range in rate constant, for ground and excited state activators alike, is the one electron oxidation potential. This correlation demands that the rate-limiting step for the ground and excited state reactions of diphenoyl peroxide and ground and excited-state activators is the same, namely, electron transfer. Thus, the supposition that radical ions produced from the peroxide and hydrocarbon are intermediates in the chemiluminescence of diphenoyl peroxide is confirmed.

Although the operation of the CIEEL mechanism was first demonstrated conclusively for dipehnoyl peroxide, many other chemiluminescent reactions have since been shown to follow this path. Some of these are discussed below.

Chemiluminescence of Dimethyldioxetanone:

The chemiluminescence of the dioxetanone ring system is somewhat more complicated than that of diphenoyl peroxide (Schmidt 1980, Adam 1979). Mainly this is because this peroxide undergoes two different reactions that are capable of generating electronically excited products. As is true of its structural cousin, dioxetane, thermolysis of dimethyldioxetanone in the absence of a suitable easily oxidized activator gives a measurable yield of electronically excited acetone. For this compound, at 30° in C₂Cl₃F₃, the yields of singlet excited



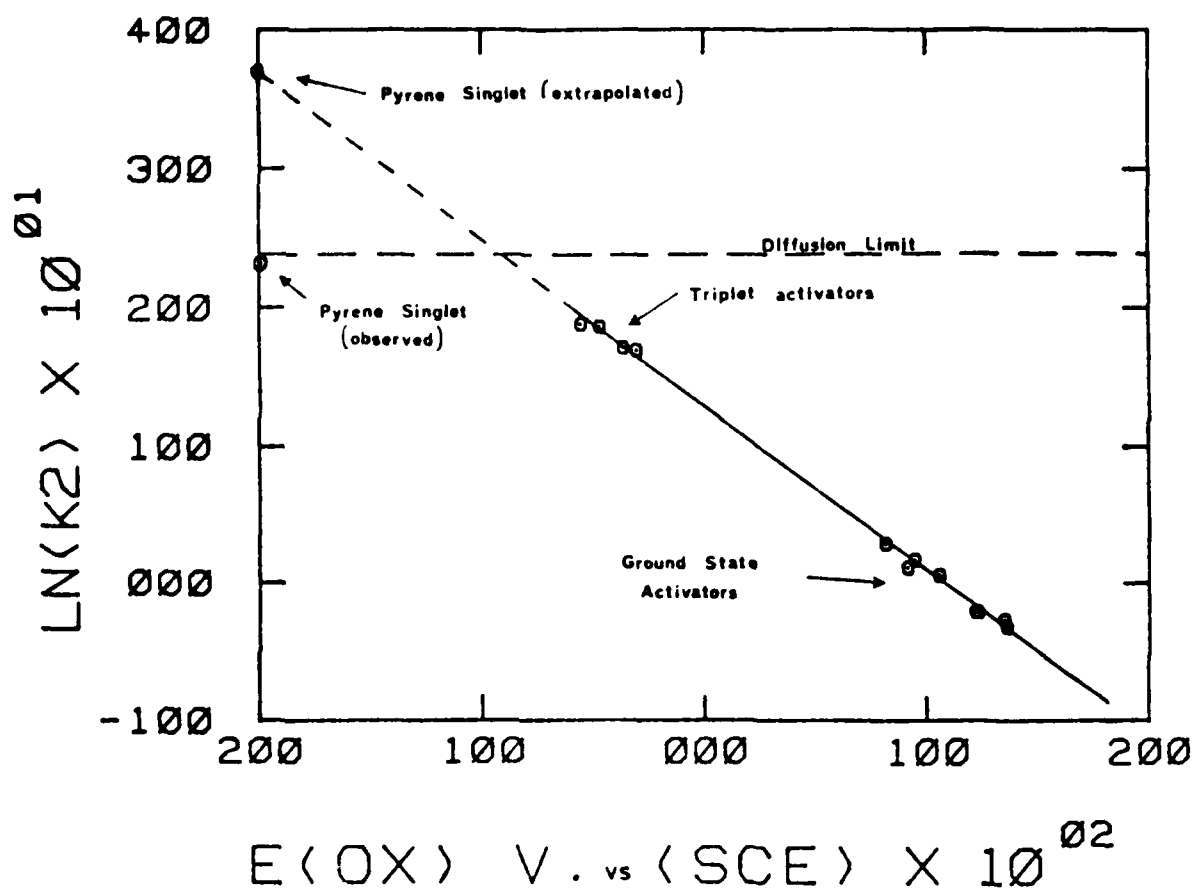


Figure 3. Correlation of reaction kinetics for the reaction of diphenoyl peroxide (2) with ground and excited state activators.

In order of increasing oxidation potential the points are: excited singlet pyrene, triplet fluoranthene, triplet anthracene, triplet 9-acetylanthracene, triplet 9,10-dibromoanthracene, rubrene, tetracene, triphenylamine, perylene, 9,10-diphenylanthracene, coronene, anthracene and pyrene.

and triplet acetone are 0.1 and 1.5% respectively. Unlike the simple dioxetanes, thermolysis of dimethyldioxetanone in the presence of an easily oxidized activator generated the electronically excited activator. The details of the mechanism of the direct and activator catalyzed luminescence of dimethyldioxetanone was probed by Schmidt and Schuster and by Adam and Cueto. The results of the study of the activator catalyzed luminescence are described herein.

As is observed for diphenoyl peroxide, rubrene catalyzes a chemiluminescent reaction of dimethyldioxetanone. However, the magnitude of k_{CAT} for the former is about 30 times that for the latter. This difference can be easily understood by analyzing equation 21. Not only is k_{CAT} sensitive to E_{ox} , but it depends also, in a straight-forward way, on E_{red} . That is, the more easily reduced is the organic peroxide the greater the magnitude of k_{CAT} with a given activator. It is well-known that diacyl peroxides are more easily reduced than peroxyesters and this fact is reflected in the magnitude of k_{CAT} . Other activators also react with dimethyldioxetanone with k_{CAT} that are related to their oxidation potentials. The initial chemiluminescence intensity (I_0) from dioxetanone and an activator can be related to k_{CAT} , the fluorescence efficiency of the activator (ϕ_f) and the initial dioxetanone ($[DMDO]_0$) and activator ($[ACT]$) concentrations according to equation 24. A plot

$$I_0/\phi_f = k_{CAT} [DMDO]_0 [ACT] \quad (24)$$

of I_0/ϕ_f against E_{ox} for a series of amine and aromatic hydrocarbon activators is shown in Figure 4. These, and other findings, led Schmidt and Schuster to postulate the mechanism shown in Figure 5 for the catalyzed chemiluminescence of dimethyldioxetanone. This mechanism is identical con-

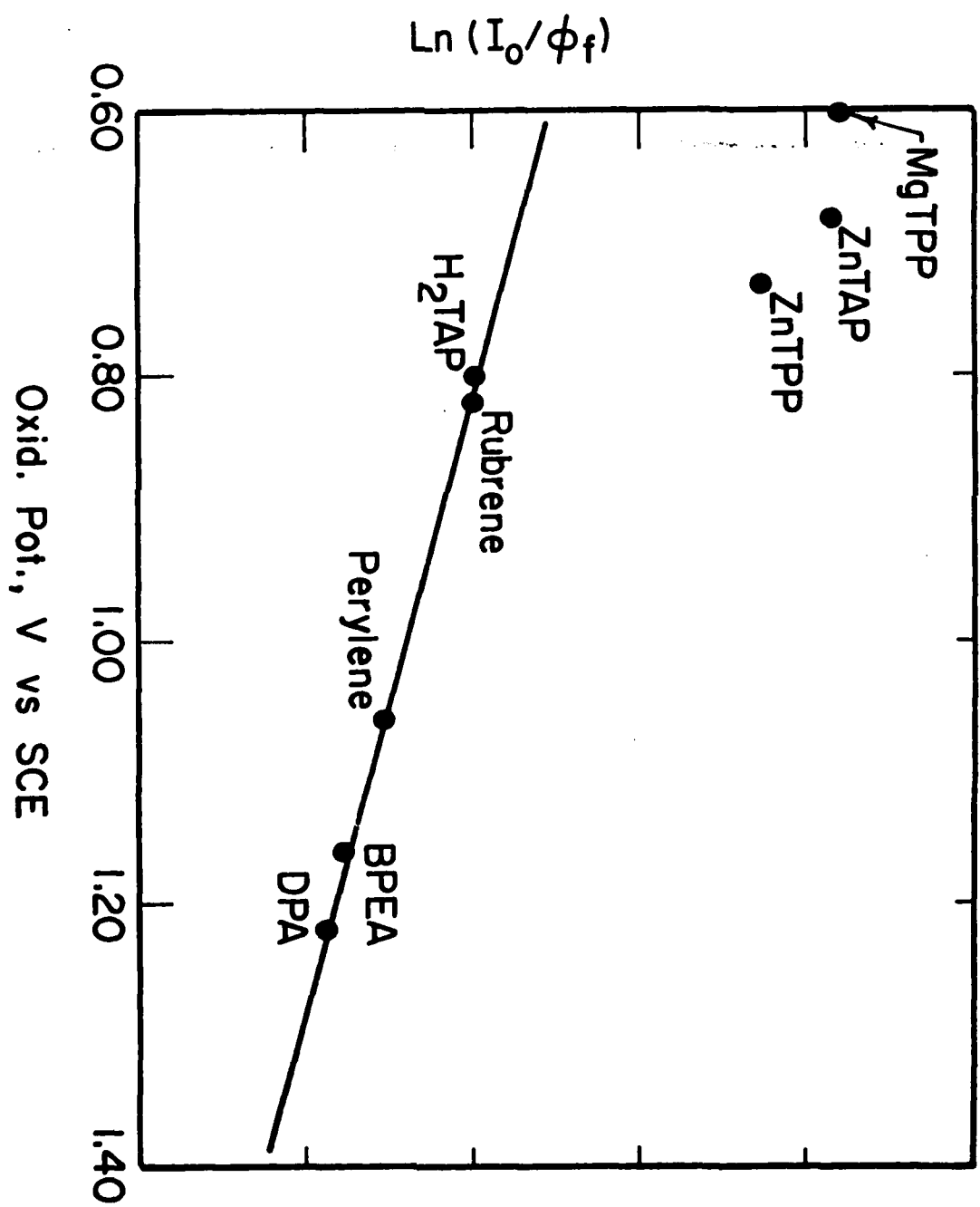
ceptually to the mechanism for diphenoyl peroxide chemiluminescence described above. The first step is the formation of an encounter complex. Activation of the encounter complex, probably by stretching the O-O bond, results in the transfer of an electron from the activator to the peroxide. Cleavage of the O-O bond ensues to generate, after loss of CO_2 , acetone radical anion and activator radical cation. Annihilation of these ions forms the excited states we detect by their emission. The rate, and thereby the efficiency of light generation, is related to the oxidation potential of the activator for a wide variety of substances. The exceptions to this correlation, shown in Figure 4, are certain metalloporphyrins.

Unusual chemiluminescent phenomena have been reported previously for metalloporphyrins. Linschitz observed emission from the thermolysis of decalin hydroperoxide and zinc tetraphenylporphyrin (ZnTPP). More recently McCapra (McCapra et. al., 1979) reported chemiluminescence from the reaction of a variety of porphyrins with ZnTPP. In both cases it was observed that the metal is a necessary requirement for chemiluminescence, but no specific function was assigned to it. Our studies have resulted in a explanation for the unusual chemiluminescent catalysis obtained for certain metalloporphyrins and dimethyldioxetanone.

The data displayed in Figure 4 show that ZnTPP, MgTPP and zinc tetraanisylporphyrin (ZnTAP) have I_0/ϕ_f one hundred to one thousand times larger than the value expected from their oxidation potentials. The value of I_0/ϕ_f is related to k_{CAT} through equation 24. As is required by this equation, the values we have determined for k_{CAT} for the unusual metalloporphyrins are 10^2 to 10^3 greater than the value expected based simply upon their oxidation potentials. Importantly, the free-base porphyrins, AgTPP, and PdTPP do not show the special catalysis.

Figure 4

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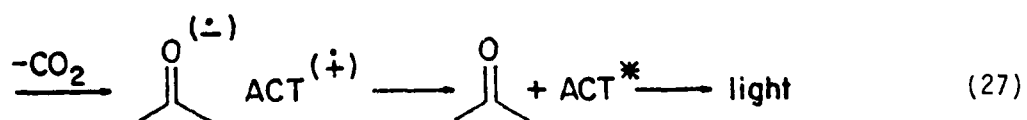
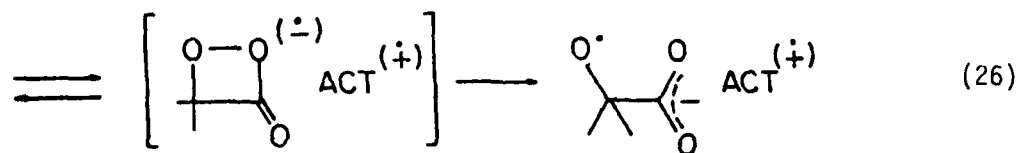
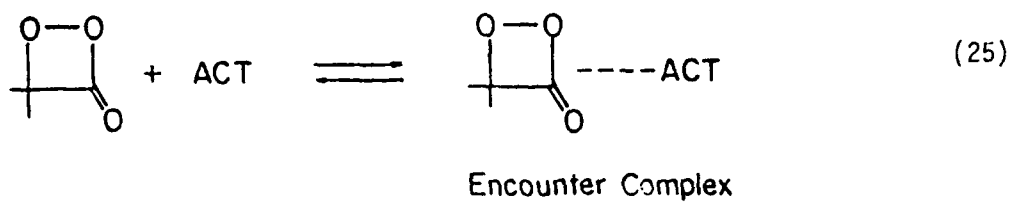


Figure 5 . The CIEEL mechanism for the thermal reaction of dimethyldioxetanone with ground state aromatic hydrocarbons (Act).

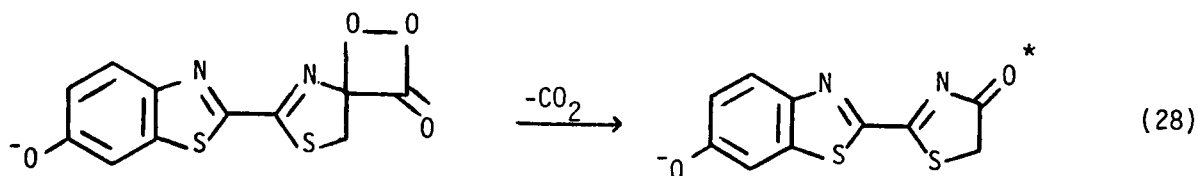
It is quite well known that certain metalloporphyrins form stable complexes with nitrogen bases such as pyridine. Moreover, it is well known that free-base porphyrins do not form these complexes. In a recent study the equilibrium constant for complex formation for metalloporphyrins and neutral oxygen donors was estimated by following the shift of the maximum of the Soret absorption band (Bogel 1977). This band shifts to longer wavelength upon complex formation. We have observed that the metalloporphyrins that exhibit the unusual catalysis, and only these metalloporphyrins, have their Soret bands shifted by tetramethyldioxetane (a model for dimethyldioxetanone). Also, we have found that the unusual catalysis can be inhibited by competitive complexation of the metalloporphyrin with neutral oxygen or nitrogen donors. Thus, when the coordination site on the metalloporphyrin is occupied by diethyl ether or pyridine, it is not nearly as effective a catalyst of dioxetanone chemiluminescence.

These observations offer an explanation of the unusual chemiluminescent catalysis of these metalloporphyrins. As shown in equation 20 the magnitude of k_{CAT} , according to the CIEEL mechanism, is the product of the equilibrium constant for complex formation (K_{12}) and the electron transfer rate constant (k_{ACT}). For the amine and hydrocarbon activators the value of K_{12} is independent of specific structure and probably depends only on diffusion of the reagents. For the metalloporphyrins, however, a special interaction leads to stabilization of the complex and hence an increase in K_{12} and the concomitant change in k_{CAT} .

While the magnesium and zinc porphyrins are among the most effective activators of chemiluminescence of dimethyldioxetanone which we have found, they are quite ineffective in catalyzing chemiluminescence with dipehnoyl peroxide. This might be surprising initially in light of the established CIEEL pathway for this peroxide. The metalloporphyrin, however, is consumed

in the reaction with diphenoyl peroxide. We suspect, therefore, that two electron reduction of this peroxide is occurring. Thus the aryloxy radical intermediate produced from the one electron reduction and O-O bond cleavage of diphenoyl peroxide is more easily reduced than the alkoxy radical derived from the one electron reduction and O-O bond cleavage of dimethyldioxetanone.

The chemiluminescent behavior observed for dimethyldioxetanone may be directly applicable to the excitation step in the bioluminescence of the firefly. The structure of the key intermediate in the firefly bioluminescence is the substituted dioxetanone shown in equation 25. In simple terms, the struc-



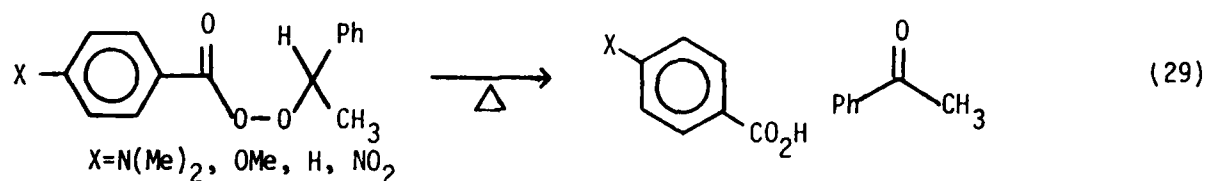
ture reveals a dioxetanone containing an easily oxidized substituent group. It has been shown that under certain circumstances substituents can serve as intramolecular electron donors for dioxetane chemiluminescence (Zaklika et. al., 1978). We have speculated that the bioluminescence of the firefly is a result of a similar intramolecular version of the CIEEL process (Koo et. al., 1978).

Secondary Peroxyesters

The basic observations about the CIEEL mechanism made above for diphenoyl peroxide and dimethyldioxetanone have been found to be directly applicable to a variety of other peroxide systems. For example, chemiluminescence from the reaction of 1-phenylethyl peroxyacetate and certain activators has been observed to proceed by the CIEEL mechanism outlined in Figure 5 (Dixon et. al., 1979). Endergonic one-electron transfer from activator to peroxide followed by O-O bond

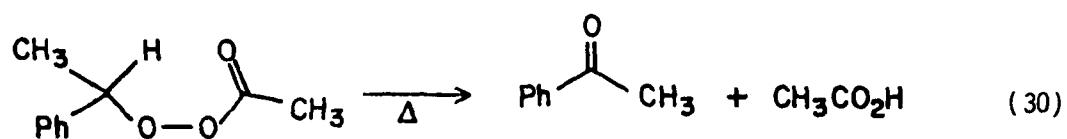
cleavage and proton transfer gives acetic acid acetophenone radical anion and activator radical cation. Annihilation of these oppositely charged radical ions leads to excited state formation and subsequent light emission.

The trend observed in the magnitude of k_{CAT} for diphenoyl peroxide and dimethyldioxetanone is carried to the peroxyester system. The reduction potential of the acyclic peroxyester is lower (more difficult to reduce) than the previously discussed peroxides, and thus k_{CAT} for a given activator is smaller for this system. This trend is seen most clearly in the series of substituted peroxybenzoates shown in equation 29. The magnitude of k_{CAT} depends greatly on



the nature of the substituent. For example, k_{CAT} in benzene at 90° for the P-NO₂ substituted perbenzoate with dimethyldihydrodibenzo[b,i]phenazine is easily measured, but for the -NMe₂ substituted case, k_{CAT} is too small to detect under these conditions. Interestingly, unlike the parent perbenzoate, the p-NO₂ substituted compound does not generate much light by the CIEEL path. This can be easily understood. The reduction potential of p-nitrobenzoic acid is more positive than that of acetophenone. Thus, we suspect that the radical anion formed after electron transfer and bond-cleavage is of the acid. Annihilation of this lower energy radical anion with the activator radical cation is not sufficiently energetic to form the emissive singlet state of the activator.

The dimethylamino substituted peroxybenzoate is also unusual. This compound is sufficiently difficult to reduce that there is no measurable catalysis even with the lowest oxidation potential activators. However, there is relatively efficient direct chemiluminescence from the excited



Activated Chemiluminescence

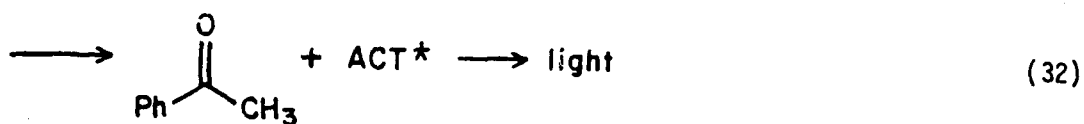
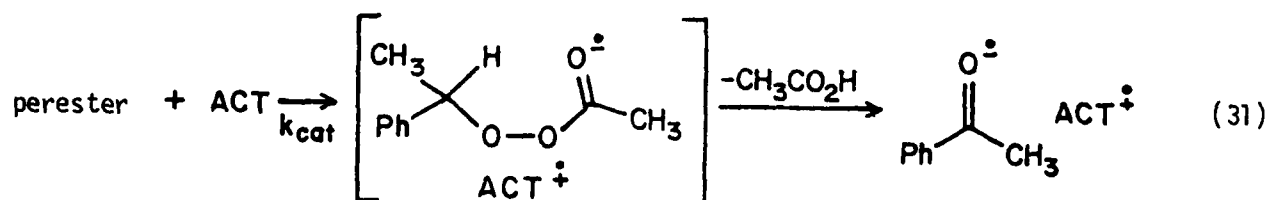


Figure 6. The CIEEL mechanism for the activated chemiluminescence of 1-phenylethylperoxy acetate (28).

singlet state of the substituted acid. The amino group is an important requirement for this chemiluminescent reaction. The yield of directly formed excited states for the parent system is much less than for the amino substituted case. While we do not yet have an exclusive explanation for this phenomenon, we do note that the same requirement of amino substitution also operates in the luminol chemiluminescent system. In this case also the excited state is a substituted benzoic acid.

Conclusions

The CIEEL path of chemiexcitation has been demonstrated to be responsible for the formation of electronically excited states from the reactions of a variety of peroxides with relatively easily oxidized fluorescers. The generality of this mechanism leads us to speculate that many of the known chemi- and bioluminescent systems have excitation processes that proceed by this path. The key requirements for efficient luminescence by the CIEEL mechanism are an easily reduced energetic peroxide that undergoes irreversible chemical transformations as the radical anion, and either an intramolecular or intermolecular electron donor with a singlet energy low enough to be accessible from the annihilation of its radical cation and the radical anion derived from the peroxide transformations.

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